III.B.6 Fundamental Reforming Studies - Role of Catalytic O_2 Supports on Fuel Reforming

Objectives

- Search for long-duration reforming catalysts in the development of auxiliary power units.
- Investigate the role of oxygen-conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon formation and/or increasing sulfur tolerance.

Approach

- Conduct catalyst characterization and evaluate catalytic hydrocarbon reforming activity for ceria-based catalysts utilizing the partial oxidation of methane (POM).
- Obtain carbon formation trends as a function of oxygen/carbon ratio and find correlation with ionic conductivity.
- Perform mechanistic studies in order to investigate the role of lattice oxygen during the POM. These tests include:
    - Catalyst labeling with $^{18}O_2$.
    - Conducting the POM reaction over $^{18}O_2$ labeled catalysts.
    - Performing prior and post reaction experiments by nuclear reaction analysis (NRA) to complement the isotopic studies and obtain ^{18}O concentration profiles and total oxygen concentration in the catalysts.

Accomplishments

- Demonstrated that catalysts with higher ionic conductivity generated less carbon and catalysts with higher reducibility showed higher conversion.

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- Confirmed by isotopic studies and by NRA that lattice oxygen oxidizes methane to generate CO and H_2 during POM.

Future Directions

Compare results obtained for ceria-based catalysts with those of mixed ionic-electronic oxide-based catalysts.

Introduction

The U.S. Department of Energy is sponsoring development of high temperature fuel cell power systems based on solid oxide technology through its Solid State Energy Conversion Alliance (SECA) program. The program is geared at mass manufacturing of fuel cells for high volume markets and multiple applications. The fuel processor is a critical component of this system and must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. There are several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell.

Ceria-based catalysts are being investigated in this work in order to fundamentally understand the role of oxygen-conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon deposition. Ceria-based catalysts have shown ability to decrease carbon formation during partial oxidation of hydrocarbons [1,2]. It has been speculated that this property is due to their high oxygen ion mobility. In this project, this assumption is investigated to elucidate a reaction mechanistic scheme to get a better understanding of carbon formation and mitigation.

Approach

Several metal-deposited catalysts were prepared for this study. Catalyst variables included metal type (Pt, Ni, Rh), support type (Al_2O_3 and CeO_2), dopant type (La, Gd, Zr) and dopant concentration (Gd 10%, Gd 30%). Characterization of ceria-based catalysts included ionic conductivity, temperature programmed reduction profiles, surface areas and catalyst phases. Catalytic activity and stability were determined. Carbon formation trends as a function of ionic conductivity and O/C ratio were obtained. Isotopic studies with ^{18}O

labeled catalysts were performed to study the reaction mechanism of the partial oxidation of methane. Tests by NRA were conducted to investigate the nature of the oxygen species participating in the POM reaction. Methane was utilized to minimize complexity of reforming operations and analysis of results.
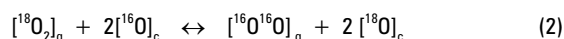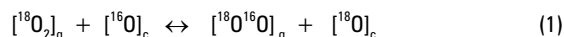
Results

Results for the first two years of this project were already included in previous reports. A brief summary is included here. Catalyst characterization was conducted in order to determine the effect of dopant addition to a ceria lattice. Ionic conductivity, catalyst reducibility and crystal phases were determined. Specifically, the addition of gadolinium to the ceria lattice showed a significant ionic conductivity enhancement. For example, at 700°C, pure ceria and gadolinium-doped ceria with 10% gadolinium concentration (GDC10) showed 2.41E-04 and 5.19E-02 S/cm, respectively. Ceria reducibility was also remarkably improved by dopant addition. Particularly, zirconia addition caused an increase in the bulk oxygen reducibility. Relative to CeO_2, the maximum reduction rate appeared at much lower temperature, about 350°C. X-ray diffraction (XRD) characterization showed peaks at $2\theta\sim28°$ and 33° characteristic of cubic ceria for most of the catalysts. In the case of zirconia-doped ceria with 50% zirconia concentration (ZDC50), this material showed broader peaks at 23° and 33.5°, indicating traces of a tetragonal phase. Catalytic activity as a function of temperature from 350 to 850°C illustrated that the light-off temperature for all catalysts was about 550°C. Above 750°C, products showed a H_2/CO ratio of about 2, and methane conversion was about 90%. Carbon deposition of several catalysts with different ionic conductivities was tested as a function of O/C ratio during the partial oxidation of methane at 700°C. Our results indicated that at low O/C ratios, the amount of carbon deposited on the surface catalyst increased. For example, at O/C=0.6, Pt/CeO_2 and Pt/ZDC50 generated 0.5 and 0.3 mg (carbon)/g catalyst, respectively. On the other hand, Pt/GDC30 and Pt/GDC10 generated about the same amount of carbon, 0.1 mg (carbon) /g catalyst. These results led to the conclusion that Pt/GDC10 and Pt/GDC30 are more resistance to carbon deposition due to their high ionic conductivity. Data regarding the effect of O/C feed ratio on the CH_4 conversion (%) during the POM reaction illustrated that for Pt/ZDC50, decreasing O/C ratio from 0.88 to 0.57 caused a decrease in CH_4 conversion of 20%.

This year, isotopic experiments were performed. Only the main results are presented here. For these tests, we preferred to use ^{18}O labeled catalysts to follow the participation of oxide oxygen in the gaseous products rather than using isotopic gaseous reactants. Briefly, catalyst labeling consisted of exposing a pre-reduced
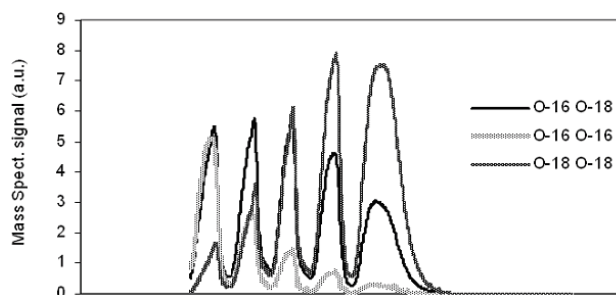

FIGURE 1. Distribution of Oxygen Species During Catalyst "Labeling" with $^{18}O_2$ Doses

catalyst to several doses of $^{18}O_2$ at 700°C. Results in Figure 1 show the mass spectrometer signal for the three oxygen species $^{16}O^{16}O$, $^{18}O^{16}O$ and $^{18}O^{18}O$ at the gas exit of the reactor. Similar results have been reported in the literature for oxygen isotopic exchange experiments with ion-conducting materials [3,4,5,6]. Based on the proposed reaction mechanisms and our results, it is suggested that the formation of $^{16}O^{18}O$ and $^{16}O^{16}O$ at the catalyst surface occurs as written below:

$$[^{18}O_2]_g \ + \ [^{16}O]_c \ \leftrightarrow \ [^{18}O^{16}O]_g \ + \ [^{18}O]_c \qquad (1)$$

$$[^{18}O_2]_g \ + \ 2[^{16}O]_c \ \leftrightarrow \ [^{16}O^{16}O]_g \ + \ 2[^{18}O]_c \qquad (2)$$

Equation 1 describes the formation of $[^{16}O^{18}O]_g$, where c indicates catalyst and g, gas phase. The formation of $^{16}O^{18}O$ occurs with the participation of one ^{18}O from the gas phase and one ^{16}O atom from the support through the oxygen exchange reaction defined as simple heteroexchange. Regarding $^{16}O^{16}O$, it is generated through the combination of a dioxygen molecule and two oxide oxygen atoms, defined as multiple heteroexchange (2). In similar experiments performed with $Ce_{0.63}Zr_{0.37}O_2$ as a function of temperature, between 30 and 600°C, Madier et al. [7] suggested that not only surface oxygen participates during the isotopic exchange reaction, but bulk oxygen atoms also are exchanged to generate the oxygen products. In a similar publication, Bedrane et al. [8] have reported that conversely to ceria, where oxygen storage capacity is only due to the surface, for zirconia-doped ceria oxides, bulk oxygen has an important role.

Experiments with $^{18}O_2$ were conducted to study the nature of oxygen species participating in the reaction of methane with oxygen to produce H_2 and CO during POM. This reaction was conducted isothermally at 700°C over ^{18}O labeled Pt/ZDC50 with a mixture of O_2 (2.5 vol%) and methane (5.0 vol%) as a function of time. Figure 2 shows results; it is observed that there are two types of carbon monoxide generated, the isotopic $C^{18}O$ and the "normal" CO. Interestingly, the rate of $C^{18}O$ formation is higher than that of CO formation at the beginning of the reaction. These results led
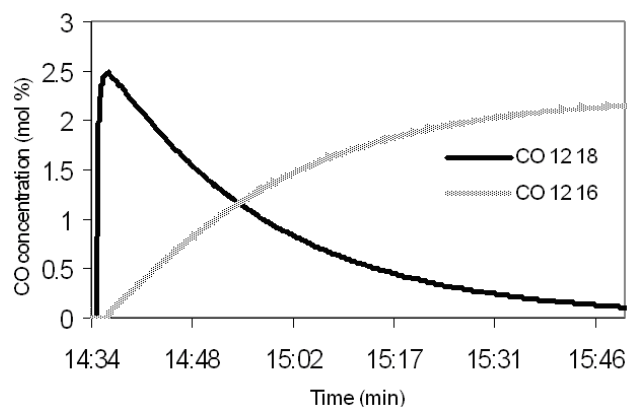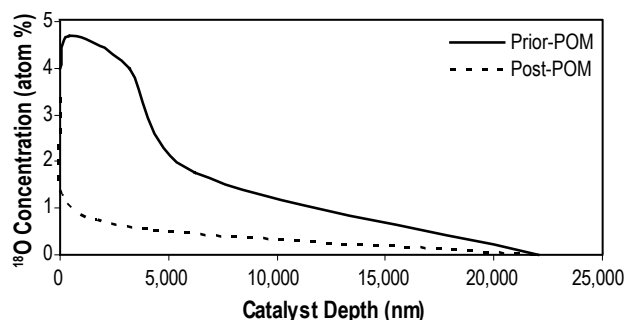
FIGURE 2. Isotopic C^{18}O and "Normal" CO Formation during the POM Reaction over ^{18}O Labeled Pt/ZDC50

FIGURE 3. ^{18}O Concentration Profiles (atom %) as a Function of Catalyst Depth (nm) for Pt/ZDC50 Prior- and Post-POM at 700°C and O/C = 1

FIGURE 4. Temperature-Programmed Isotopic Exchange over Pt/ZDC50 - Maximum Isotopic Exchange Occurred at 530°C

to the conclusion that CO formation does not occur in the gas phase, and there is strong evidence of the participation of oxygen originating from the catalyst. It is worth mentioning that the H$_2$/CO product ratio was 2 during the complete test (the concentration of H$_2$ is not included in this graph).

Spent catalysts from the POM reaction were analyzed by nuclear reaction to determine ^{18}O oxygen concentration as a function of depth profile. Specifically, ^{18}O labeled Pt/ZDC50 samples prior- and post-POM reaction were tested by using the ^{18}O(p,α)15N nuclear reaction. In this experiment, the samples were bombarded with 0.74 MeV H$^+$ ions. The energy of α particles generated by the nuclear reaction was 3.25 MeV, and the surface barrier detector at 135° scattering angle was used to measure the α particles generated. Results are presented in Figure 3 for catalysts prior- and post-POM reaction. It is immediately obvious that the concentration of ^{18}O in every channel is significantly lower in the post-POM sample than in the fresh (prior-POM) sample. This result is strong evidence that the oxygen specie from the lattice reacts with methane to generate CO^{18} and is replenished from the molecular ^{16}O oxygen initially present with the incoming methane in the gas phase.

Temperature-programmed isotopic exchange reactions with ^{18}O labeled Pt/ZDC50 were performed. Specifically, these reactions were conducted between ^{16}O in the gas phase and the labeled catalyst. Results showed that below 150°C, the oxygen exchange was negligible. At higher temperatures, the exchange rate increased steadily, showing a single maximum peak (530°C) for the formation of the main product, ^{16}O^{18}O, as illustrated in Figure 4. The formation of ^{16}O^{18}O is a function of the dissociation, incorporation, and diffusion steps. Since the ^{16}O^{18}O molecule occurs only after the dissociation of the oxygen molecule, we believe that the dissociation step is faster than the incorporation and migration of surface oxygen to the catalyst bulk.
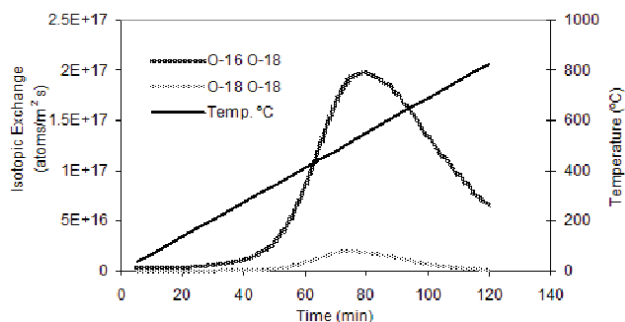
Conclusions

- Dopant addition significantly enhanced the reducibility and ionic conductivity of pure ceria.
- Catalysts with higher ionic conductivity mitigate carbon deposition.
- Catalysts with higher reducibility showed higher catalytic activity.
- Isotopic studies and post reaction tests by nuclear reaction analysis revealed that CO formation does not occur directly with oxygen in the gas phase during the partial oxidation of methane and that lattice oxygen is the oxygen specie participating in this reaction. Lattice oxygen is replenished from the gas phase.

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1. Salazar, Maria; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Catalytic partial oxidation of methane over Pt/ceria-doped catalysts: effect of ionic conductivity. Applied Catalysis A: General 310 (2006) 54–60.

2. Salazar-Villalpando, Maria D.; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Celik, Ismail; Synthesis gas by partial oxidation and the role of oxygen-conducting supports: A review. Fuel Cell Science, Engineering and Technology, 2004, June 14-16, 2004, Rochester, New York USA, Fuel Cell. 2004, p. 681-690.

Presentations

1. Salazar, Maria; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Role of Lattice Oxygen in the Partial Oxidation of Methane over Rh & Pt/Zirconia-Doped Ceria. Mechanistic aspects. Accepted for presentation at the ACS Fall meeting 2006.

2. Salazar-Villalpando, Maria D.; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Floyd, Donald; Catalytic Partial Oxidation of Methane on Rh-Ceria Based Catalysts. Effect of Reducibility. Presented at AICHE Fall meeting, 2005.

3. Salazar-Villalpando, Maria D.; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Synthesis Gas by Partial Oxidation and the Role of Oxygen-Conducting Supports: A Review. Presented at the Second International Conference on Fuel Cell Science, Engineering and Technology, June 16, 2004.